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**Note**

# Synthesis of xanthons: Part 11†—Synthesis of 4-methylpyrano[2,3-*b*]xanthone

Shubhangi S Soman* & K N Trivedi‡
Chemistry Department, Faculty of Science,
M S University of Baroda, Baroda 390 002

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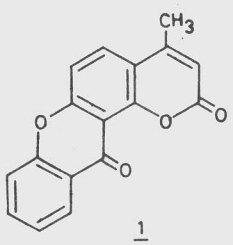
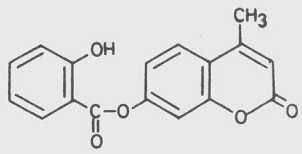
4-Methylpyrano[2,3-*b*]xanthone has been prepared by thermal condensation of 7-hydroxy-4-methylcoumarin with ethyl salicylate in diphenyl ether.

We have reported[1] from our laboratory the thermal condensation of 7-hydroxy-4-methylcoumarin with ethyl salicylate in diphenyl ether to give 4-methylpyrano[2,3-*a*]xanthone **1**, m.p. 280°. As the compound **1** was sparingly soluble in common organic solvents its $^1$H NMR spectra could not be recorded at that time and the structure **1** was tentatively assigned to it on the basis that the 8-position of 7-hydroxy-4-methylcoumarin derivatives is more reactive than the 6-position and that almost all reactions are taking place regiospecifically at position-8. Further, Konde Deshmukh *et al.*[2] when carried out the above condesation in refluxing diphenyl ether, they recovered only the starting materials. However, they synthesised **1** by a different route (m.p. 259°).

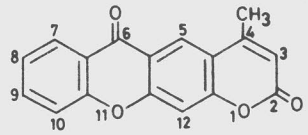
In view of this contradictory report, we repeated the thermal condensation of 7-hydroxy-4-methylcoumarin with ethyl salicylate in diphenyl ether. The reaction mixture was refluxed for 18 hr, and diphenyl ether was Steam-distilled. The crude product was treated with dil. NaOH solution to remove starting materials and the residue was chromatographed on silica gel. Elution of the column with benzene gave two products. The product, m.p. 179° which came out first was assigned (4-methyl-7-coumarinyl)salicylate structure **2** on the basis of IR and $^1$H NMR specta. IR: 1730 (lactonyl >C=O) and 1690 cm$^{-1}$ (ester >C=O): $^1$H NMR ($CDCl_3$): δ 2.4 (d, 3H, *J*=1.2 Hz, $C_4$-$CH_3$), 6.15 (q, 1H, *J*=1.2 Hz, $C_3$-H), 6.8 (d, 1H, *J*=9 Hz, $C_5$-H), 6.95 (dd, 1H, *J*=9 Hz, 1.2 Hz, $C_6$-H), 7.1 (d, 1H, *J*=1.2 Hz, $C_8$-H), 7.3-7.5 (m, 3H, Ar-H), 7.9 (dd, 1H, *J*=9, 1.2 Hz, $C_6$-H), 10.2 (s, 1H, $C_2$-OH). The second product, m.p. 272°, was assigned linear structure 4-methylpyrano[2,3-*b*]xanthone **3** on the basis of IR and $^1$H NMR spectra. IR: 1740 (lactonyl >C=O) 1660 cm$^{-1}$ (xanthonyl >C=O), $^1$H NMR ($CDCl_3$+DMSO-$d_6$): δ 2.58 (d, 3H, *J*=1.2 Hz, $C_4$-$CH_3$), 6.35 (q, 1H, *J*=1.2 Hz, $C_3$-H), 7.4 (s, 1H, $C_{12}$-H), 7.45-7.85 (m, 3H, $C_8$-H, $C_9$-H, $C_{10}$-H), 8.3 (dd, 1H, *J*=9, 1.2 Hz, $C_7$-H), 8.57 (s, 1H, $C_5$-H). If the compound **3** had the angular pyranoxanthone structure **1**, then the down field signlet at δ 8.57 would have been absent. The linear pyranoxanthone **3**, m.p. 269° (incorrectly named as 4-methylcoumarinoxanthone) has been synthesised by Konde Deshmukh *et al.*[3] by a different route. Our spectral data is almost identical with that reported by them.



**1**



**2**



**3**

The formation of **3** can be explained by assuming that ethyl salicylate first undergoes transesterification to give **2** which on thermal Fries rearrangement followed by ring closure yieds **3**. When **2** alone is refluxed in diphenyl ether, it also gives **3** which confirms the above route for the formation of **3**. The formation of linear pyranoxanthone **3** is a novel observation as it does not obey the regiospecificity of 7-hydroxycoumarin derivatives to position-8.

†Part 10: Patel G N & Trivedi K N, *Indian J Heterocyclic Chem*, 5, **1996**, 249.

‡Expired on November 25, 1996

## Experimental

$^1$H NMR spectrum of **2** was recorded on R-32, Perkin Elmer 90 Mhz instrument while that of **3** was recorded on Brucker 200 Mhz instrument using TMS as internal standard and IR spectra on a R-408 Schimadzu spectrophotometer.

7-hydroxy-4-methylcoumarin (5.0 g, 0.0311 mole), ethyl salicylate (10 mL) were refluxed in diphenyl ether (10 mL) for 18 hr. Diphenyl ether and unreacted ethyl salicylate were removed by steam-distillation. The product was washed with dil. NaOH (0.1 *N*, 200 mL) which on acidification gave unreacted 7-hydroxy-4-methylcoumarin (1.5 g). The crude product (5 g) was purified by column chromatography using benzene as an eluent. First five elutions (5×500 mL) gave condensed ester **2**, yield 1.8 g, m.p. 179° (Found: C, 69.13; H, 4.26. $C_{17}H_{12}O_5$ requires C, 68.92; H, 4.05%); Next elution with benzene gave the pyranoxanthone **3**, yield 0.75 g, m.p. 272° (Found: C, 73.42; H, 3.65. $C_{17}H_{10}O_4$ requires C, 73.38; H, 3.59%).

Ester **2** (2.0 g) was refluxed in diphenyl ether (8 mL) for 10 hr. Diphenyl ether was removed by steam-distillation. The product was washed with dil. NaOH and water. The crude product was purified by column chromatography using benzene as eluent to give **3**, yield 0.65 g.

### Acknowledgement

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### References

1 Patolia R J & Trivedi K N, *Indian J Chem*, 22B, **1983**, 444.
2 Konde Deshmukh R S & Paradkar M V, *Indian J Chem*, 28B, **1989**, 968.
3 Konde Deshmukh R S & Paradkar M V, *Synth Commun*, 24, **1994**, 659.